1,3-, and 1,4-) fall on the line defined by eq 9. This supports the concept that the N–I$_2$ bonds are directional and largely covalent and that no di-coordination of I$_2$ is involved.

6. Lone-pair/lone-pair repulsion in pyridazine (1,2-diazine) is lost or reduced in reactions 1 and 2. This is an important contributor to its enhanced (relative to the other diazines) GB[56] and IB. At variance with this, protonation of pyrazole is followed by the formation of two adjacent, mutually repelling N–H$^+$ bonds.[56] The energy of this repulsion is estimated at 6.5 kcal·mol^{-1}. Figure 2 reveals that the only significantly deviant datum from eq 9 is in pyrazole which has an IB that seems "too large". In fact, it has the value that would correspond to pyrazole were its PA some 6.0 kcal·mol^{-1} higher. It is clear that although some charge is drained from the lone pair of the nitrogen, the repulsion between the N–H and N–I$_2$ bonds is proportionally much smaller than that between the two N–H$^+$ bonds. Also, as suggested by one of the referees, a hydrogen-bonding effect is possible; it would correspond to the (resonance structure extreme) N···I$^+$—I$^-$···HN. This would occur only here, of all the bases used, owing to the proximity of the basic site with an adjacent hydrogen bond donor site.

III. Conclusion

1. "Gas-phase-like" structural effects can be observed in solution chemistry.

2. The comparison of gas-phase and solution basicities under conditions of small charge dispersal leads to valuable insights in the field of structure–reactivity relationships.

IV. Experimental Section

1-*tert*-Butylimidazole[57] and 1-adamantylimidazole[58] have been synthesized by methods previously described. The remaining bases were commercial products of the highest purity available. All these compounds have been carefully purified by standard methods. In all cases, the structures were confirmed by spectroscopic techniques (MS, IR, NMR).

Solvents of spectrograde quality were refluxed over and distilled from sodium (*n*-C$_7$H$_{16}$) or P$_4$O$_{10}$ (CCl$_4$, CH$_2$Cl$_2$).

Equilibrium constants K_c for reaction 2 are the average of at least six different measurements.

The absence of I$_3^-$ was carefully checked. Experiments were performed at 25.0 and 30.0 °C on a Cary 219 spectrophotometer using matched 1-cm silica window cells. Temperature was kept constant within 0.1 °C by a Lauda S-15 thermostat.

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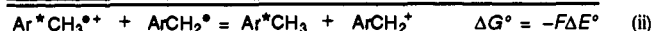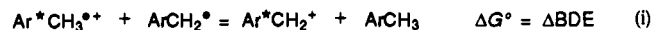
Electrode Potentials and the Thermodynamics of Isodesmic Reactions

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Abstract: The free energies of isodesmic reactions can be calculated from appropriate electrode potential differences without the necessity of evaluating reference electrode potentials or the free energies of any chemical or physical processes. Class I reactions involve different oxidation states of the same species while reactions involving different species at the same oxidation state level are grouped in Class II. The free energy change of H$^\bullet$ exchange (i) above the double line is equal to that for electron transfer (ii) below the double line. The first aryl group appearing on both sides of the equations is designated with an asterisk

$$\text{Ar}^*\text{CH}_3{}^{\bullet+} \; + \; \text{ArCH}_2{}^\bullet \; = \; \text{Ar}^*\text{CH}_2{}^+ \; + \; \text{ArCH}_3 \qquad \Delta G^\circ = \Delta \text{BDE} \qquad \text{(i)}$$

$$\overline{\text{Ar}^*\text{CH}_3{}^{\bullet+} \; + \; \text{ArCH}_2{}^\bullet \; = \; \text{Ar}^*\text{CH}_3 \; + \; \text{ArCH}_2{}^+} \qquad \Delta G^\circ = -F\Delta E^\circ \qquad \text{(ii)}$$

for clarity, i.e. the compositions of Ar* and Ar are identical. Similar equations relate differences in acid dissociation constants to an appropriate electrode potential difference. For class II reactions, an electrode potential difference can be related to the sum of the free energies of two isodesmic reactions involving the transfer of atoms, ions, or groups. The Cr–H bond dissociation energies of chromium hydride complexes which have recently been evaluated experimentally were selected as standard processes for the evaluation of other BDE. The reversible oxidation of the 2,6-di-*tert*-butyl-4-nitrophenoxide ion was used to relate thermochemical quantities determined in acetonitrile to those in dimethyl sulfoxide.
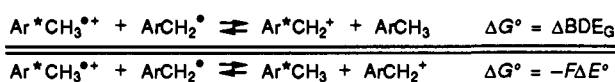
Introduction

Thermochemical cycles incorporating electrode potentials often provide a means of obtaining reliable estimates of thermodynamic quantities that are either difficult or sometimes impossible to obtain directly. There has been a recent surge of activity in this area to obtain equilibrium and bond energy information in a variety of different systems. A seminal effort in this area by Breslow

established the use of thermochemical cycles to estimate pK_a values of weak carbon acids in aprotic solvents as well as equilibrium constants for the dissociation of alcohols to carbenium ions.[2] Arnold devised three different thermochemical cycles to estimate
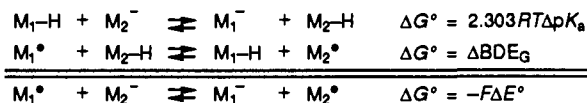
(1) (a) Utah State University. (b) On leave from the Department of Chemistry, University of Kashmir (India). (c) Present address: Chiron Laboratories, Trondheim, Norway. (d) University of Oslo.

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Scheme I

$$Ar^*CH_3^{\bullet+} + ArCH_2^{\bullet} \rightleftharpoons Ar^*CH_2^{+} + ArCH_3 \qquad \Delta G^{\circ} = \Delta BDE_G$$

$$\overline{\overline{Ar^*CH_3^{\bullet+} + ArCH_2^{\bullet} \rightleftharpoons Ar^*CH_3 + ArCH_2^{+} \qquad \Delta G^{\circ} = -F\Delta E^{\circ}}}$$

Scheme II

$$M_1-H + M_2^{-} \rightleftharpoons M_1^{-} + M_2-H \qquad \Delta G^{\circ} = 2.303RT\Delta pK_a$$

$$M_1^{\bullet} + M_2-H \rightleftharpoons M_1-H + M_2^{\bullet} \qquad \Delta G^{\circ} = \Delta BDE_G$$

$$\overline{\overline{M_1^{\bullet} + M_2^{-} \rightleftharpoons M_1^{-} + M_2^{\bullet} \qquad \Delta G^{\circ} = -F\Delta E^{\circ}}}$$

pK_a values of cation radicals in solution.[3] Bordwell employed thermochemical cycles involving carbanion oxidation potentials and the pK_a's of the corresponding acids to obtain cation radical pK_a's and C–H bond dissociation energies (BDE).[4] Parker developed thermochemical cycles to estimate dication pK_a's as well as those of anion radical and dianion conjugate acids.[5] Similar cycles were proposed by Tilset to estimate metal–hydride BDE and pK_a's of metal–hydride cation radicals.[6] Griller and Wayner have emphasized the generality of such cycles for inter-relating the thermochemistry of molecules, radicals, and their ions.[7] Arnett has shown that the difference in energies of homolytic and heterolytic bond cleavage can be obtained from the appropriate electrode potential difference for reduction of carbenium ions and oxidation of carbanions.[8]

In this paper we use electrode potential differences to determine free energy changes in isodesmic reactions, i.e. those in which the number of chemical bonds remain constant. Using free energy and electrode potential differences removes a number of assumptions and approximations necessary when single electrode potentials are used in thermochemical cycles. On the other hand, the free energy differences obtained must be related to free energy changes of half-reactions by having one known free energy change of each type reaction treated. The thermochemical cycles applied by both Breslow[2] and Bordwell[4] involve isodesmic reactions but were not referred to as such.

Results and Discussion

Classes of Isodesmic Reactions. We will consider two classes of isodesmic reactions for which thermochemical parameters can be derived using electrode potentials. Reactions between two different oxidation states of the same molecular species are grouped in Class I while reactions between two different species are Class II reactions.

(a) Class I Reactions. The free energy change of a Class I reaction can be calculated directly from the electrode potential change for the electron transfer between the reactants. The notation that we use in this paper is that we write the isodesmic reactions above and the corresponding electron exchange reactions below a double line. The free energy changes above and below this double line are equal. The notation used for a typical Class I reaction is illustrated in Scheme I. The free energy change for the reaction above the double line is equal to the difference in bond dissociation energies (ΔBDE_G) of the methylarene and the cor-

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Scheme III

$$\Delta G^{\circ}$$

$$M-H(sol) \rightleftharpoons M^{-}(sol) + H^{+}(sol) \qquad 2.301RTpK_a \qquad (1)$$

$$M^{-}(sol) \rightleftharpoons M^{\bullet}(sol) + e^{-} \qquad -FE^{\circ}_{ox}(M^{-}, sol) \qquad (2)$$

$$H^{+}(sol) \rightleftharpoons 0.5H_2(g) \qquad FE^{\circ}(H^{+}, sol) \qquad (3)$$

$$0.5H_2(g) \rightleftharpoons H^{\bullet}(g) \qquad \Delta G^{\circ}_f(H^{\bullet}, gas) \qquad (4)$$

$$H^{\bullet}(g) \rightleftharpoons H^{\bullet}(sol) \qquad \Delta G^{\circ}_{sol}(H^{\bullet}, sol) \qquad (5)$$

$$\overline{\overline{M-H(sol) \rightleftharpoons M^{\bullet}(sol) + H^{\bullet}(sol) \qquad BDE \qquad (6)}}$$

$$BDE = 2.301pK_a + F[E^{\circ}_{ox}(M^{-}, sol) - E^{\circ}(H^{+}, sol)] +$$
$$\Delta G^{\circ}_f(H^{\bullet}, g) + \Delta G^{\circ}_{sol}(H^{\bullet}, sol) \qquad (7)$$

$$H^{+}(aq) + e^{-} \rightleftharpoons 0.5H_2(g) \qquad (8)$$

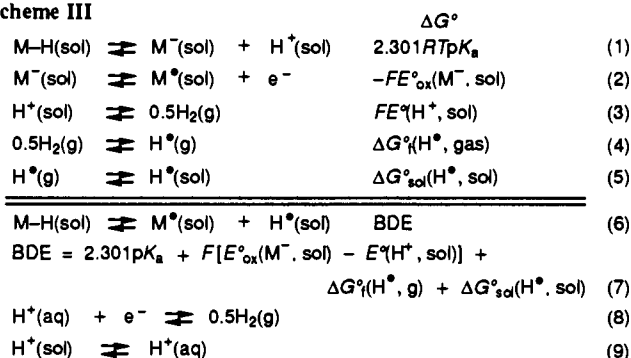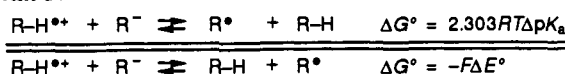$$H^{+}(sol) \rightleftharpoons H^{+}(aq) \qquad (9)$$

Table I. Reference Electrode Potentials, Free Energies of Transfer of the Proton, Solvation Parameters for Hydrogen Atom, and Calculated Constants for Thermochemical Cycles

	reference electrode			
	$(H^{+}/H_2)_{AN}$	NHE	$(H^{+}/H_2)_{DMSO}$	NHE
solvent	AN	AN	DMSO	DMSO
E_{ref},[a] eV	0.477	0	-0.195	0
ΔG°_{tr},[a,b]	not used	-11.1	not used	4.50
$\Delta G^{\circ}_{solv}(H^{\bullet})$,[b,c]	5.12	5.12	5.7	5.7
$\Delta S^{\circ}_{solv}(H^{\bullet})$,[c] eu	-11.9	-11.9	-12.0	-12.0
$T\Delta S^{\circ}(H^{\bullet})$,[b,d]	-4.62	-4.62	-4.59	-4.59
C_G[e]	53.7	42.7	54.2	58.7
C_H[e]	58.3	47.2	58.9	63.4

[a] Data from ref 9. [b] kcal/mol. [c] Data from ref 12. [d] At 298.15 K, $\Delta S^{\circ} = S^{\circ}_f(H^{\bullet}) + \Delta S^{\circ}_{solv}(H^{\bullet}) = 15.5$ eu (AN) for 15.4 eu (DMSO). [e] $C_G = \Delta H_f(H^{\bullet}) + \Delta G^{\circ}_{solv}(H^{\bullet})$; $C_H = C_G - T\Delta S^{\circ}(H^{\bullet})$.

responding cation radical. The subscript G indicates that the BDE are free energies. The free energy change for the electron exchange reaction can be equated to the difference in reduction potentials of the cation radical and $ArCH_2^{+}$.

(b) Class II Reactions. These reactions involve the transfer of atoms, ions, or groups between two different molecular species. The electron exchange reaction written below the double line in this case is the sum of two isodesmic reactions involving the transfer of a fragment in different oxidation states. This is illustrated in Scheme II for the transfer of hydrogen atoms and protons between metal hydrides and metal anions and radicals. If either ΔpK_a or ΔBDE_G is known, the other quantity can be obtained by equating the free energies above and below the double lines.

Uncertainties in Single Electrode Potential Thermochemical Cycles. Before discussing the use of the relationships for isodesmic reactions a review of the uncertainties in the use of single electrode potential thermochemical cycles, which are the alternative to the isodesmic reaction relationships, is in order.

A pertinent example of this type of cycle is that used to estimate bond dissociation energies[4,6] illustrated in Scheme III for metal hydrides. Equations 1–5 above the double line represent a closed cycle, the sum of which is the bond dissociation energy of M–H in solution (reaction 6). Reference electrode reaction 3 is for the reduction of H^{+} in the solvent to which all other reactions are referred. This could be substituted for using two equations, (8) for the normal hydrogen electrode and (9) for the transference of H^{+} from the solvent to water. The electrode potentials for the reduction of H^{+} have been reported in a number of commonly used electrochemical solvents such as acetonitrile (AN) and dimethyl sulfoxide (DMSO).[9]

The uncertainties that we must be concerned with, in addition to those arising from experimental errors in the determination of the electrode potentials and the pK_a of M–H, are those associated with process 5 and in relating (3) to (9). The uncertainty in the latter conversion is that in ΔG°_{tr} for the transfer of H^{+} from the solvent to water. Since the electrode potentials for reaction 2 are measured in solvent containing electrolyte it is this solution that

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Scheme IV

$$R-H^{\bullet+} + R^- \rightleftharpoons R^\bullet + R-H \qquad \Delta G^\circ = 2.303RT\Delta pK_a$$

$$R-H^{\bullet+} + R^- \rightleftharpoons R-H + R^\bullet \qquad \Delta G^\circ = -F\Delta E^\circ$$

the free energy of transfer refers to and this cannot be expected to be the same as that referring to the pure solvent. It is possible that the presence of electrolyte affects both ΔG_{tr} and the electrode potentials and that these errors cancel. The free energy of solvation of the hydrogen atom [eq 5, $\Delta G^\circ_{sol}(H^\bullet,sol)$] is not known in any solvent. This has been taken to equal the free energy of solvation of the hydrogen molecule.[4,6] Clearly, there is no sure way to assess the degree of uncertainty in this term.

It is convenient to gather all of the constants which contribute to the uncertainty into one term, C, and transform eq 7 to eq 10. The value of C depends upon the solvent and the reference
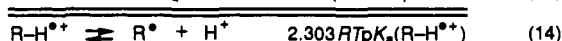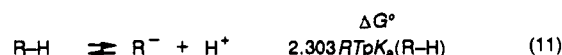
$$BDE = 2.301RTpK_a + FE^\circ_{ox}(M^-,sol) + C \qquad (10)$$

electrode to which $E^\circ_{ox}(M^-,sol)$ is referred. The various parameters from which C is derived in AN and DMSO are summarized in Table I. Two different reference electrodes are considered, the $(H^+/H_2)_{sol}$ is the hydrogen electrode in the solvent and the NHE is the normal hydrogen electrode in water. Neither of these reference electrodes are used in practice. For this reason, we suggest using the $(Fc/Fc^+)_{sol}$ system where Fc refers to ferrocene as the reference when applying electrode potentials in thermochemical cycles. The justification for this is that the $(Fc/Fc^+)_{sol}$ are known[9] in the common electrochemical solvents. The use of other reference electrodes such as the saturated calomel electrode gives rise to still another source of uncertainty of unknown magnitude.

Two values of C, C_G, and C_H are listed in Table I for each reference electrode system. The subscripts refer to whether the derived BDE are free energy (G) or enthalpy (H) values. The two constants differ by the free energy of the hydrogen atom in the solvent.[10] The two potential scales given for each solvent differ by the free energy of transfer of the proton from the solvent to water (ΔG°_{tr}). The only additional quantity not given in Table I necessary to derive the C values is the free energy of formation of the hydrogen atom in the gas phase $[\Delta G^\circ_f(H^\bullet,gas)]$ which is equal to 48.58 kcal/mol.[12]

It is clear from the foregoing discussion that there is a high degree of uncertainty, of unknown magnitude, in the parameters that are used in the single electrode potential thermochemical cycles. Yet, BDE determined using the cycles are reasonably close to literature values. Bordwell[4h] has recently concluded that the agreement observed between BDE derived from thermochemical cycles and experimental data is the result of a fortuitous cancellation of errors. We agree with this conclusion and suggest that setting up the reactions of interest in terms of equilibria of isodesmic reactions is a convenient method to derive the ΔBDE or ΔpK_a from electrode potential measurements.

Class I Isodesmic Reactions. The relationship illustrated in Scheme IV allows ΔpK_a, the difference in pK_a between a cation radical and the neutral substrate, to be determined directly from the appropriate electrode potential difference. The relationship between Scheme IV and the thermochemical cycle (eqs 11–14) used by Bordwell[4a] to determine pK_a values of organic cation radicals is obvious.

				ΔG°	
R–H	$\rightleftharpoons$	R^-	+ H^+	$2.303RTpK_a(R-H)$	(11)
R^-	$\rightleftharpoons$	$R^\bullet$	+ e^-	$FE^\circ(R^\bullet)$	(12)
$R-H^{\bullet+}$	+ e^- $\rightleftharpoons$	$R-H$		$-FE^\circ(R-H^{\bullet+})$	(13)
$R-H^{\bullet+}$	$\rightleftharpoons$	$R^\bullet$	+ H^+	$2.303RTpK_a(R-H^{\bullet+})$	(14)

Table II. Reversible Anion Oxidation Potentials, pK_a Values, and Cr–H Bond Dissociation Energies of Cr–H Complexes in Acetonitrile

	Cr–H complex	
	$(\eta^5\text{-}C_5H_5)Cr(CO)_3H)$	$(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_3)H)$
$E_{ox}(Cr^-)$, V vs $(Fc/Fc^{\bullet+})^a$	-0.688	-1.289
pK_a	13.3[b]	21.8[c]
BDE, kcal/mol	61.5[d]	59.8[d]
C_{Fc},[e] kcal/mol	59.2	59.8

[a] Reversible electrode potential for the oxidation of the anion determined in this study. [b] Values determined in acetonitrile from ref 13. [c] Determined in this study with Norton's method referred to in footnote *b*. [d] Value from ref 14. [e] Constant derived for eq 10 with electrode potentials referenced to $Fc/Fc^{\bullet+}$.

Class II Isodesmic Reactions. The relationship of most interest for this class of reactions is that illustrated by Scheme II which interrelates differences in pK_a, BDE, and electrode potentials. In order for this scheme to be useful to determine new parameters it is necessary to have a standard system for which all of these parameters have been determined experimentally. We select the reactions of the metal hydride Cr–H complexes in acetonitrile as a standard system. The data necessary for Scheme II are summarized in Table II.

The oxidations of the corresponding anions of both Cr–H complexes in acetonitrile are chemically reversible at low voltage sweep rates. The pK_a of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ has been reported by Norton[13] and we have used their method to determine the pK_a of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_3)H$ in acetonitrile. Attempts to determine the pK_a of the Cr–H complexes in DMSO failed due to side reactions of the hydrides.

A major advantage to using the Cr–H complexes as standard systems, in addition to the fact that reversible potentials for the oxidation of Cr^- could be determined and the pK_a are known, is that these are among the few compounds for which accurate values of the BDE based on direct measurements are known, in this case for the chromium–hydrogen bond. Reliable calorimetry values for Cr–H BDE have recently been reported by Hoff.[14]

The thermochemical cycle illustrated in Scheme II results in eq 15 for calculating any one of the three energy differences providing that two of them are known. It is somewhat less con-

$$-F(E^\circ_1 - E^\circ_2) = $$
$$2.303RT[(pK_a)_1 - (pK_a)_2] - [(BDE_G)_1 - (BDE_G)_2] \quad (15)$$

venient to use (15) directly than to apply (10). Therefore, C in (10) was evaluated using data for our standard systems which is equivalent to using (15). Since our electrode potentials are referred to $Fc/Fc^{\bullet+}$ we defined our empirically determined constant as C_{Fc}. Since our standard BDE are enthalpy values and these are the most commonly discussed, values obtained using C_{Fc} in (10) are enthalpy values. The values of C_{Fc} in AN determined in this way, 59.2 and 59.8 kcal/mol (Table II) should be compared to the value given in Table III (59.4 kcal/mol) derived from the thermochemical data in Table I.

A limitation of our standard Cr–H systems is that we were unable to use these standards in DMSO. This is a serious limitation since DMSO has been the medium of choice for the study of pK_a of carbon acids.[15] This problem is readily solved by using the isodesmic relationship (Scheme II) to determine the pertinent BDE of any substance for which pK_a are available in both solvents, and it is possible to obtain reversible oxidation potentials for the

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(10) It is necessary to estimate the entropy of the hydrogen atom in the solvent. This is taken to be equal to the sum of the entropy of formation of the hydrogen atom in the gas phase (27.4 eu)[11] and the entropy of solvation of hydrogen molecule (-11.4 eu).[12]

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Table III. Reversible Anion Oxidation Potentials, pK_a Values, and Calculated O–H Bond Dissociation Energy of 2,6-Di-*tert*-butyl-4-nitrophenol in Acetonitrile and Dimethyl Sulfoxide

	solvent	
	acetonitrile	DMSO
$E_{ox}(ArO^-)$, V vs $(Fc/Fc^{\bullet+})^a$	0.057 ± 0.005	0.126 ± 0.005
E_{Fc/Fc^+}, V vs NHE	0.528	0.537
pK_a $(ArOH)^b$	19.0	7.6
BDE,^{c} kcal/mol	86.7	
C_{Fc}, kcal/mol	59.5^d	73.5^e

^{a} Anion oxidation potentials measured in solvent/Bu_4NPF_6 (0.1 M) in the presence of excess Et_4NOH. ^{b} Values from ref 16. ^{c} Calculated with eq 10 with C_{Fc} = 59.5 kcal/mol derived from the data in Table II. ^{d} Empirical value, average of those in Table II. ^{e} Empirical value, obtained with eq 10 and the thermochemical data in this table.

Table IV. Comparison of Values of Constants Derived for Thermochemical Cycles To Determine Bond Energies

solvent	C^a	$C_{Fc}(exptl)^b$
acetonitrile/Bu_4NPF_6 (0.1 M)	59.4	59.5^c
DMSO/Bu_4NPF_6 (0.1 M)	75.8	73.5

^{a} Constant in kcal/mol for electrode potentials referred to $Fc/Fc^{\bullet+}$, obtained by adjusting the NHE values in Table I to account for the $Fc/Fc^{\bullet+}$ potentials in AN (0.528 V) and in DMSO (0.537 V). ^{b} The experimental data are from Tables II and III, in kcal/mol. ^{c} This is the average of values obtained with use of the two different Cr–H complexes.

corresponding anion. These criteria are fulfilled by 2,6-di-*tert*-butyl-4-nitrophenol (ArOH). The pK_a of ArOH in both AN and
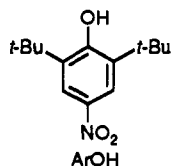
ArOH

DMSO have been reported.[15] We find that ArO⁻ is oxidized reversibly at low sweep rates during cyclic voltammetry in both AN and DMSO. Data pertaining to ArOH in both solvents are summarized in Table III.

The O–H BDE of ArOH was determined to be equal to 86.7 kcal/mol using the electrode potential and pK_a data in Table III in conjunction with eq 10. The reversible potentials for the oxidation of ArO⁻ are referred to the $Fc/Fc^{\bullet+}$ couple. Although electrode potentials are commonly related to the NHE, this is an unnecessary and perhaps undesirable exercise when using eq 10 with C derived from the energetics in (15). This source of confusion is eliminated by defining C_{Fc} with electrode potentials referenced to $Fc/Fc^{\bullet+}$. In doing so, C_{Fc} is equal to 59.5 (AN) and 73.5 (DMSO) kcal/mol in the two solvents. The value of C_{Fc} in DMSO was derived using the $E_{ox}(ArO^-)$, pK_a, and BDE (86.7 kcal/mol) data in eq 10.

It is of interest to compare the empirically determined values of C with those derived from thermochemical data. The comparison (Table IV) shows that C_{Fc} determined in acetonitrile/Bu_4NPF_6 (0.1 M) differs by only 0.1 kcal/mol from that calculated from thermochemical data (Table I) for the pure solvent. A larger discrepancy (2.3 kcal/mol) was observed for C_{Fc} in DMSO/Bu_4NPF_6 (0.1 M). The difference in C_{Fc} in the two solvents suggests that the free energy of transfer of H^+ between AN and DMSO is the dominating factor.

Bond dissociation energies of hydrocarbon C–H acids calculated using (10) for pK_a and anion oxidation potentials reported in DMSO[4b] are summarized in Table V. The BDE values in parentheses are literature values listed in ref 4b. The BDE determined with C_{Fc} equal to 73.5 kcal/mol differ very little (+0.2 kcal/mol) from those reported earlier.[4b] The most likely reaction of the free radicals generated during oxidation of the hydrocarbon anions is dimerization. Self-reaction $(2R^{\bullet} \rightarrow$ products) rates have been determined[17] for a number of radicals of this type, and it

Table V. Hydrocarbon C–H Bond Dissociation Energies, Acid Dissociation Constants, and Electrode Potentials in Dimethyl Sulfoxide Solvent

R–H	pK_a	E_{ox}/V^a	BDE^b/kcal mol^{-1}		
			uncorrected	corrected	lit.
An–CH$_2$–H^c	31.1	−1.489	81.6	84.1 ± 0.5	(81.8 ± 1.5)
Ph$_2$C–H	32.3	−1.540	82.0	84.5 ± 0.5	$(80.4–84)$
Ph$_3$C–H	30.6	−1.486	81.0		(>75)
Cp–H^d	18.0	−0.722	81.4	83.9 ± 0.5	$(81.2–82.9)$
In–H^e	20.1	−0.950	79.0	81.5 ± 0.5	(84 ± 3)
Fl–H^f	22.6	−1.069	79.7	82.2 ± 0.5	(80 ± 5)

^{a} Anion oxidation potentials from ref 4b vs $Fc/Fc^{\bullet+}$. ^{b} C–H bond dissociation energies calculated with eq 10 with C_{Fc} = 73.5 kcal/mol. The column labeled "corrected" assumes a +109 $\pm$ 20 mV correction of E_{ox} which corresponds to an EC(dim) mechanism with log k = 9 $\pm$ 1 M^{-1} s^{-1}. The uncertainty in the rate constants gives rise to $\pm$1.2 kcal mol^{-1} error in BDE. The ranges of values in parentheses are those listed in ref 4b from the literature. ^{c} An = 9-anthracenyl. ^{d} Cp = cyclopentadienyl. ^{e} In = indenyl. ^{f} Fl = 9-fluorenyl.

Table VI. Anion Oxidation Potentials, Acid Dissociation Constants, and M–H BDE of Metal Hydrides in Acetonitrile

	compound	$E°_{ox}(M^-)^a$	pK_a^b	BDE^c
1	$(\eta^5$-$C_5H_5)Cr(CO)_3H$	−0.688	13.3	61.5^d
1a	$(\eta^5$-$C_5H_5)Cr(CO)_2(PPh_3)H)$	−1.289^e	21.8^e	59.8^d
2	$(\eta^5$-$C_5H_5)Mo(CO)_3H$	−0.501	13.9	69.2
3	$(\eta^5$-$C_5Me_5)Mo(CO)_3H$	−0.709	17.1	68.5
4	$(\eta^5$-$C_5H_5)W(CO)_3H$	−0.491	16.1	72.3
5	$(\eta^5$-$C_5H_5)W(CO)_2PMe_3H$	−1.225	26.6	69.6
6	$Mn(CO)_5H$	−0.555	14.1	68.0
7	$Mn(CO)_4PPh_3H$	−0.870	20.4	68.4
8	$Re(CO)_5H$	−0.690	21.1	74.7
9	$(\eta^5$-$C_5H_5)Fe(CO)_2H$	−1.352	19.4	57.1
10	$(\eta^5$-$C_5H_5)Ru(CO)_2H$	−1.057	20.2	64.9
11	$Fe(CO)_4H_2$	−0.403	11.4	67.6
12	$Co(CO)_4H$	−0.271	8.3	66.4
13	$Co(CO)_3P(OPh)_3H$	−0.489	11.3	65.2
14	$Co(CO)_3PPh_3H$	−0.723	15.4	65.0

^{a} Electrode potentials vs $Fc/Fc^{\bullet+}$ from ref 6a (not corrected for kinetic potential shifts). ^{b} pK_a data from Norton and co-workers.[17] ^{c} Calculate with eq 10, C_{Fc} = 59.5 kcal/mol. ^{d} Values from ref 14. ^{e} Determined in this study.

appears that log k = 9 $\pm$ 1 would give an appropriate kinetic correction for all radicals other than triphenylmethyl in Table V. For example, sterically hindered pentamethylcyclopentadienyl underegoes dimerization at near diffusion control, i.e. 2×10^9 M^{-1} s^{-1}.[18] This gives rise to a 109 mV kinetic contribution to the oxidation potential which has been taken into account in the column labeled "corrected". The correction is based upon the equations in Scheme VI for the EC(dim) mechanism. Since triphenylmethyl cation is reduced reversibly during cyclic voltammetry in DMSO at low sweep rates,[2b] no correction is necessary for a kinetic potential shift. We estimate the maximum deviation from log k = 9 to be $\pm$1 for the other radicals in Table V which acknowledges the possibility of $\pm$0.5 kcal/mol error in the derived BDE due to uncertainty in the electrode potentials brought about by kinetic shifts. Correction of irreversible electrode potentials for kinetic contributions is discussed in more detail below.

Errors Associated with Thermochemical Data Obtained with Equation 10. The expected error in BDE derived using eq 10 depends upon the precision in pK_a and electrode potentials used as well as the uncertainty in C_{Fc}. The uncertainty in C_{Fc} derived using $E_{ox}(ArO^-)$ vs. $Fc/Fc^{\bullet+}$ (Table III) arises from the uncertainty in the experimentally determined BDE for Cr–H which amounts to $\pm$1 kcal/mol.[14] The uncertainties in Cr–H pK_a ($\pm$0.1 pK unit)[13] and our errors in the measurement of anion oxidation potentials ($\pm$0.005 V, 0.1 kcal/mol) are insignificant. Uncertainties in relative BDE for a series of compounds, as exemplified

(17) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200 and references cited therein.

(18) Davies, A. G.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. II* **1981**, 692.

Scheme V. The EC Mechanism

$$A + e^- \rightleftharpoons B \quad (16)$$

$$B \longrightarrow products \quad (17)$$
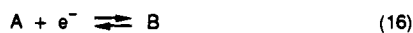
$$\Delta E_p/(mV) = (E_{1/2} - E_p)^{rev} - 780(RT/F) + (RT/2F)\ln[(RT/F)(k/\nu)] \quad (18)$$

$$\Delta E_p/(mV) = -38.4 + 12.85\ln(k/\nu)] \quad (at\ 298.15\ K) \quad (19)$$

$$dE_p/d\log\nu = 29.6\ mV/decade;\ dE_p/d\log C_A = 0 \quad (at\ 298.15\ K) \quad (20)$$

Table VII. Kinetic Peak Potential Shifts for First-Order and Second-Order Reactions of Electrode-Generated Intermediates[a]

	electrode mechanism	
k	first-order (EC)[b] ΔE_p, mV (kcal/mol)	second-order (EC(dim))[c] ΔE_p, mV (kcal/mol)
10^{10}	287.1 (6.6)	128.3 (3.0)
10^8	227.9 (5.3)	88.8 (2.1)
10^6	168.7 (3.9)	49.3[d] (1.1)
10^4	109.5 (2.5)	9.9 (0.2)
10^2	50.4[d] (1.2)	

[a] Theoretical LSV peak potential shifts for measurements at 298 K, $\nu = 0.1$ V/s at a substrate concentration of 1.0 mM. [b] Calculated with eq 19 in the text. [c] Calculated with eq 24 in the text. [d] Checked by digital simulation to verify the conversion of equations.

by the series of metal hydrides (M–H) in Table VI, depend upon the precision in electrode potentials. Rate constants were either available or estimated for the dimerization of M• formed during oxidation of M−.[6a] The electrode potentials were corrected for the kinetic potential shifts before applying eq 10 with C_{Fc} equal to 59.5 kcal/mol. The maximum error estimated for the oxidation potentials of this series of anions was ±0.02 V which corresponds to an error in relative BDE of ±0.5 kcal/mol. This includes both the experimental error in the potential measurement and possible errors in the estimation of rate constants for the dimerization of radicals formed during oxidation.

Effect of Linear Sweep Voltammetry Kinetic Peak Shifts on Electrode Potential Measurements. Reversible electrode potentials, required for the rigorous use of eq 10, are often inaccessible. Neglect of kinetic shifts of peak potentials obtained by linear sweep voltammetry (LSV) can give rise to significant errors in derived thermochemical quantities. For example, if the electrode generated intermediate is undergoing an irreversible first-order reaction (Scheme V) with a rate constant equal to 10^{10} s^{-1}, the peak potential measured at 298 K at a voltage sweep rate (ν) of 0.1 V/s differs from the reversible peak potential by 287 mV. This corresponds to a 6.6 kcal/mol error in any thermochemical quantity derived from the irreversible peak potential. Kinetic peak potential shifts ($\Delta E_p = E_p^{obs} - E_p^{rev}$) as a function of first-order rate constants for reaction 17 calculated using eq 19[17] are listed in Table VII. A first-order rrate constant equal to 10^2 s^{-1} under the above conditions gives rise to ΔE_p equal to 50 mV which translates to 1.2 kcal/mol in thermochemical quantities. Kinetic potential shifts for the related ECE mechanism are 9 mV greater than those for the EC mechanism (Scheme V). The effect of irreversible chemical reaction 17 on the LSV response gives rise to the relationships in (20), i.e. E_p shifts 29.6 mV/decade change in ν and is independent of the substrate concentration (C_A).

Homogeneous chemical reactions following charge transfer which are second order in the product of the electrode reaction give rise to smaller ΔE_p. The second-order dimerization mechanism (Scheme VI) exemplifies second-order reactions. At $C_A = 10^{-3}$ M, a second-order rate constant of 10^{10} M^{-1} s^{-1} for reaction 21 gives rrise to $\Delta E_p = 128$ mV (3 kcal/mol) at 298.15 K and $\nu = 0.1$ V/s. The EC(dim) mechanism is particularly relevant to this paper since this is the most common reaction pathway of free radicals formed upon oxidation of the corresponding anions. The kinetic shift data are summarized in Table VII. For this mechanism E_p shifts 19.7 mV for a decade change in either ν or C_A (eq 25).

Two different strategies can be adopted to minimize the error due to ΔE_p. The first approach is to estimate the rate constant of the homogeneous follow-up reaction and make the appropriate

Scheme VI. The EC(dim) Mechanism

$$A + e^- \rightleftharpoons B \quad (21)$$

$$2B \longrightarrow dimer \quad (22)$$
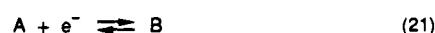
$$\Delta E_p/(mV) = (E_{1/2} - E_p)^{rev} - 902(RT/F) + (RT/3F)\ln[(2RT/3F)(kC^\circ_A/\nu)] \quad (23)$$

$$\Delta E_p/(mV) = -29.6 + 8.57\ln(kC^\circ_A/\nu) \quad (at\ 298.15\ K) \quad (24)$$

$$dE_p/d\log\nu = 19.7\ mV/decade;\ dE_p/d\log C_A = 19.7\ mV/decade \quad (at\ 298.15\ K) \quad (25)$$

Table VIII. Linear Sweep Voltammetry Peak Potentials for Quasireversible Charge Transfer Compared to Those of the Reversible Process

log Λ[a]	$\nu_{relative}$[b]	E_p, mV	$(E_p - E_p^{rev})$, mV
∞		28.5	0
1.5	0.1	29.2	0.7
0.7	4	33.4	4.9
0.3	25	40.6	12.1
−0.1	158	56.7	28.2
−0.5	1000	87.0	58.5

[a] Λ is a dimensionless heterogeneous rate constant. Data from: Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113. [b] Arbitrarily assigned so that at $\nu = 0.1$ V/s there is an insignificant error in E_p (0.7 mV).

correction while the second is to increase the voltage sweep rate in order to diminish the effect of the kinetic step on the peak potential. In principle either method can provide the reversible peak potential required in eq 10; however, there are problems associated with both procedures.

In order to make a correction for ΔE_p it is necessary to know both the mechanism, or at least the reaction order in electrode generated intermediate (B), and the rate constant for the reaction that B undergoes during the recording of the linear sweep voltammogram. This implies that detailed voltammetric studies are necessary for each and every electrode peak potential measurement. The importance in knowing the pertinent mechanism is obvious from comparing the peak potential data for the EC with that for the EC(dim) mechanism (Table VII). However, distinguishing between first-order and second-order reactions of B is straightforward from the relationships in eqs 21 and 25.[18]

The second strategy involves diminishing ΔE_p by increasing ν. There are two possible pitfalls in this approach. It has been shown that errors in E_p due to uncompensated resistance are minimal for LSV measurements in solvents such as AN at microelectrodes as long as ν is no greater than about 1 V/s.[18] However, substantial errors can be encountered at higher ν, and compensating for this error is not always a precise procedure. The other pitfall is just as serious. Most E_p measurements of interest in the context of this paper are on quasi-reversible charge trnasfer processes. The response of these systems frequently approaches that of Nernstian systems at iow sweep rates, and errors in E_p associated with the charge-transfer process are of the order of a few millivolts which is negligible in terms of the overall error expected in the thermochemical quantities. However, increasing ν has the effect of greatly amplifying this error. The data in Table VIII show that if E_p for a quasireversible process is shifted 0.7 mV from that of the Nernstian charge transfer (E_p^{rev}) at a voltage sweep rate of 0.1 V/s, E_p of the same systems is expected to differ by 58.5 mV from E_p^{rev} at 1000 V/s. The latter shift corresponds to an error of 1.35 kcal/mol in derived thermochemical quantities.

It is our opinion that the most reliable method to minimize error due to ΔE_p is to carry out LSV studies at low ν and then apply a correction based upon a rate constant for the follow-up reaction, which may be either determined or estimated. In any event it should be possible to assess the uncertainty brought about by ΔE_p.

Second harmonic AC voltammetry (SHAC) is another experimental method that can provide reversible electrode potentials.[19] However, interpretation of experimental results is besieged

(19) (a) McCord, T. G.; Smith, D. E. *Anal. Chem.* **1969**, *41*, 1423. (b) Bond, A. M.; Smith, D. E. *Anal. Chem.* **1974**, *46*, 1946.

with similar problems to those encountered in LSV studies, but in this case, in the frequency domain. For the EC mechanism, the relationship between first-order rate constant and the frequency (ω) necessary to avoid the effects of the chemical follow-up reaction is given by $k < 3\omega$. In the extreme case where k is equal to 10^{10} s^{-1}, ω must be of the order of 3×10^{10} s^{-1} to "out-run" the homogeneous chemical reaction. Since the highest practical values of ω are on the order of 2×10^5 s^{-1}, reversible potentials of very short lived intermediates are inaccessible by this technique. Furthermore, quasireversible charge transfer gives rise to phase shifts that make it virtually impossible to obtain E^{rev} when high ω are required. It is therefore necessary to keep these limitations in mind and to interpret SHAC results with great care. Some of the practical aspects of the measurement of reversible electrode potentials using SHAC have been described.[20]

Conclusions

Our data support the conclusion[4h] that the agreement between gas-phase BDEs and those from eq 10 using C derived from thermochemical data results from a fortuitous cancellation of errors. Nevertheless, the empirical method gives BDEs that are within experimental error of those obtained by use of (10) with C_{Fc} derived from reliable BDEs (Scheme II), which provides a means of accurately estimating BDE from pK_a and electrode potential data.

Experimental Section

Instrumentation and Data Acquisition. The potentiostat was a JAS Instruments Systems Model J-1600-B driven by a Hewlett-Packard HP 3314A function generator. Data were recorded using a Nicolet Model 310 digital oscilloscope with 12-bit precision. The oscilloscope and the function generator were controlled by a PC-AT via a GPIB interface. Trigger periods were selected to minimize interference by line noise.[21] The current–voltage curves were passed through a Stanford Research Systems Model SR640 low-pass filter to remove high-frequency noise. Data acquisition, including fast Fourier transform filtering, and manipulation were accompanied with use of FORTRAN programs.[22] Electrode potentials were evaluated by derivative cyclic voltammetry.[23]

Materials. Reagent grade acetonitrile was distilled from P$_2$O$_5$ before passing through a column of active neutral alumina to remove water and protic impurities. Dimethyl sulfoxide was distilled under vacuum before use. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane–ether before use. 2,6-Di-*tert*-butylphenol was used as received (Aldrich). 2,6-Di-*tert*-butyl-4-nitrophenol was prepared according to a literature procedure.[24]

Preparation of [CpCr(CO)$_2$(PPh$_3$)$^-$]PPN$^+$. Cr(CO)$_3$(NCMe)$_3$ was prepared by heating Cr(CO)$_6$ (220 mg, 1.0 mmol) in acetonitrile (15 mL) for 48 h. The solvent was removed by vacuum transfer, and the residue was dissolved in THF (15 mL). NaCp·DME[25] (178 mg, 1.0 mmol) was added, and the solution was heated at reflux for 6 h. The solution was cooled at ambient temperature and HBF$_4$·Et$_2$O (150 μL, 1.0 mmol) was added. After the addition of PPh$_3$ (262 mg, 1.0 mmol), the solution was heated at reflux for 20 h. The presence of CpCr(CO)$_2$(PPh$_3$)H was indicated by IR spectroscopy:[26] ν_{CO} 1920, 2005 cm^{-1}; ν_{CrH} 1793 cm^{-1}. The solvent was removed in vacuo. The residue was dissolved in acetonitrile, and potassium *tert*-butoxide (112 mg, 1.0 mmol) was added. The solvent was removed by vacuum transfer after the solution was stirred for 30 min, and the residue was dissolved in THF (10 mL). PPN$^+$Cl$^-$ (574 mg, 1.0 mmol) was added, and the solution was stirred for 24 h. The solution was filtered through Celite and the solvent was removed to provide a red oil. Crystallization from acetone/ether gave the product as dark red crystals (419 mg, 49% based on Cr(CO)$_6$). ^{1}H NMR (DMSO-d_6) δ 3.93 (s, 5 H), 7.1–7.8 (m, 45 H); IR (acetonitrile) ν_{CO} 1700, 1755 cm^{-1}.

Determination of the pK_a of CpCr(CO)$_2$(PPh$_3$)H (CrH). Mixtures of [CpCr(CO)$_2$(PPh$_3$)$^-$]PPN$^+$ (Cr$^-$) and a buffer system made up from excess pyrolidine (B) and pyrolidinium tetrafluoroborate (BH$^+$) were dissolved in acetonitrile. KBr IR solution cells (path 0.1 mm) were filled with the solutions, and the CrH:Cr$^-$ ratio was determined from the IR (ν_{CO}) spectra of the solutions. Three different runs with independently prepared solutions containing different buffers yielded pK_a = 21.8 ± 0.1 using eq 16 and the literature value for pK_a(BH$^+$) = 19.6.[27] The procedure used was similar to that previously described[13] featuring the evaluation of [B] and [BH$^+$] from the total concentration of base added, taking into account the known[27] association constant of BH$^+$ with B.

$$pK_a(CrH) = pK_a(BH^+) - \log\{[Cr^-][BH^+]/[CrH][B]\} \quad (26)$$

(20) Ahlburg, E.; Parker, V. D. *Acta Chem. Scand.* **1980**, *B34*, 91.
(21) Equations 18 and 23 were adapted from equations in: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; Chapter 6.
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